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THE COMBUSTION OF THE SALTS OF TETRAAMINE COPPER (II)

V. V. Gorbunov, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

THE COMBUSTION OF THE SALTS OF TETRAAMINE COPPER (II)

V. V. Gorbunov and L. F. Smagin
(Moscow)

In [1] it was shown that the combustion rate of amines of copper (II), nickel (II) and cobalt (III) is 15-20 times higher than that of nitrates of these same amines.

Investigated in this research work was the combustion of complex salts of tetraamine copper (II) (TAM) with the general formula

$$[Cu(NH_3)_4](An)_2,$$

where

$$An - BrO_3^-;\ ClO_3^-;\ ClO_4^-;\ MnO_4^-;\ NO_3^-;\ NO_2^- \text{ и } JO_3^-.$$

Complex salts produced by the method similar to that described in [2] were also analyzed for copper and ammonia content. The charges used had a relative density of not less than 0.90, and were pressed into plexiglass tubes with a diameter of 7 or 4 mm. The experiment was conducted in a bomb with a constant pressure in a nitrogen atmosphere under pressures up to 100 atm(gage). The

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Translator's note: The complex chemical compounds listed in this article appear to be ligands, and the term "amine" transliterated exactly from the Russian could actually be "ammine." Also, the chemical element J in the Russian is I (iodine).

combustion rate was measured with a photorecorder. The thermal stability of the complex salts was estimated according to the delayed flash time ($\tau_{зад}$) of an 0.05 g tared sample at a temperature of 280°C.

The experimental results and calculations of the heat and combustion temperature are presented in a table and in a figure.

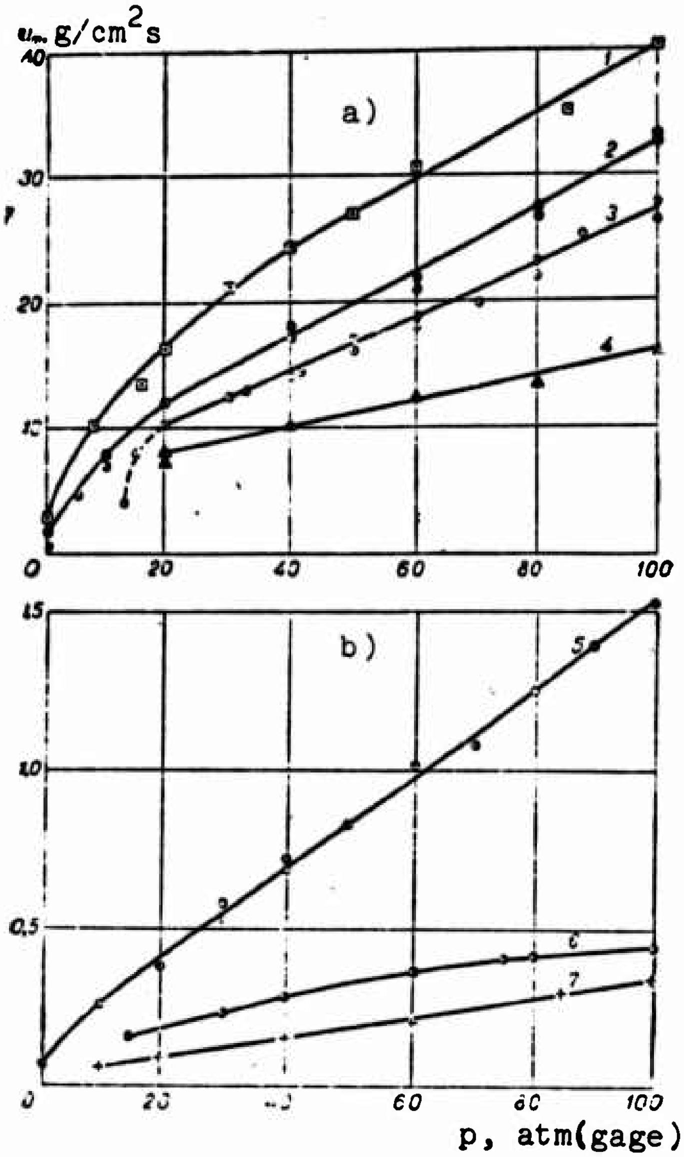
In the investigated range of pressures the highest combustion rate is exhibited by the bromate of TAM. At pressures of 20-100 atm(gage) the chlorate and perchlorate of TAM are close according to combustion rate and are second only to the bromate of TAM in this respect. The bromate, chlorate and perchlorate of TAM burn at atmospheric pressure at rate of 3.0, 1.8 and 0.6 g/cm^2·s, respectively. The permanganate of TAM begins to burn at 8 atm(gage); at higher pressures its combustion rate is almost one-half less than that of perchlorate. The nitrate, nitrite and iodate of tetraamine copper burn at a considerably slower rate. Only the nitrate of these salts burns at atmospheric pressure (u_m = = 0.7 g/cm^2·s); nitrites and iodates begin to burn at 15 and 10 atm(gage), respectively.

An intense flash with a sharp noise was observed for complex salts of BrO_3^-, ClO_3^- and ClO_4^-, a weak flash with a dark-red luminescence for MnO_4^-; nitrate and nitrite of TAM decompose with a release of oxides of nitrogen, iodate-iodine vapors. The most stable is $[Cu(NH_3)_4](MnO_4)_2$, which at normal temperature decomposed with the formation of a loose residue consisting of CuO and MnO_2. Apparently, the decomposition of this salt also occurred during synthesis, as a result of which the purity of the obtained product turned out to be low (95.5%).

Based on the combustion rate the studied complex salts can be classified into two groups: rapid-burning - with anions of BrO_3^-, ClO_3^-, ClO_4^- amd MnO_4^- whose combustion rate at 100 atm(gage)

Formula of the salt	Product purity, wt.%	$-\Delta H^{0}_{298}$ of formation kcal/mole	Combustion reaction equation	Heat of combustion kcal/mole	Heat of combustion kcal/kg	Calc. combustion temperature	U_m, g/cm^2·s at 100 atm (gage)	$\tau_{зад}$, s at 280°C
$[Cu(NH_3)_4](BrO_3)_2$	98,0	133	$=\underset{(г)}{CuBr}+\underset{(г)}{6H_2O}+\underset{(г)}{0{,}5Br_2}+2N_2$	200	516	2150	40,5	Less than 1 s
$[Cu(NH_3)_4](ClO_3)_2$	98,5	145	$=\underset{(г)}{CuCl}+\underset{(г)}{6H_2O}+0{,}5Cl_2+2N_2$	196	657	2100	33	..
$[Cu(NH_3)_4](ClO_4)_2$	99,5	158	$=\underset{(г)}{CuCl}+\underset{(г)}{6H_2O}+O_2+0{,}5Cl_2+2N_2$	183	555	1950	27	42 ±3
$[Cu(NH_3)_4](MnO_4)_2$	95,5	355	$=\underset{(ж)}{Cu}+\underset{(ж)}{0{,}66Mn_3O_4}+\underset{(г)}{5{,}34H_2O}+0{,}44NH_3+1{,}78N_2$	152	412	1500	16	Less than 1 s
$[Cu(NH_3)_4](NO_3)_2$	99,5	198(3)	$=\underset{(ж)}{Cu}+\underset{(г)}{6H_2O}+3N_2$	154	605	1750	1,5	44±2
$[Cu(NH_3)_4](NO_2)_2$	99,0	148	$=\underset{(тв)}{Cu}+\underset{(г)}{4H_2O}+1{,}33NH_3+2{,}33N_2$	98	437	1350	0,44	5
$[Cu(NH_3)_4](JO_3)_2$	99,0	212	$=\underset{(г)}{CuJ}+\underset{(г)}{0{,}5J_2}+\underset{(г)}{6H_2O}+2N_2$	107	225	1480	0,34	3

*The enthalpies of the formation of complex salts (apart from nitrate) were determined by the method of comparative analysis based on the ΔH of formation of a complex salt and the corresponding simple salt taken from [3, 4].



The dependence of the combustion rate of salts of tetra-amine copper (II), on the pressure. a) rapid-burning anions: 1 - BrO_3^-, 2 - ClO_3^-, ClO_4^-, 4 - MnO_4^-; b) slow-burning salts of anions: 5 - NO_3^-, 6 - NO_2^-, 7 - IO_3^-.

falls within the range 40-16 $g/cm^2 \cdot s$, and slow-burning salts - with anions of NO_3^-, NO_2^- and IO_3^- whose combustion rates at this same pressure are 1.5-0.34 $g/cm^2 \cdot s$; that is, by 1-2 orders less. The indicated difference holds even at lower pressures.

A comparison of the combustion rates and computed combustion temperatures of the rapid- and slow-burning complex salts indicated that the latter have a lower combustion temperature. The exception is the rapid-burning $[Cu(NH_3)_4](MnO_4)_2$, whose combustion temperature (1500°K) is lower than the slow-burning nitrate

(1750°K). It is obvious that in this case the lesser combustion temperature is compensated for by a significantly higher oxidizing action of the permanganate-ion (or products of its decomposition) in comparison with the nitrate-ion. The thermal stability of the complex salts does not indicate a substantial effect on its combustion rate: in the rapid-burning group there are unstable salts of ClO_3^-, BrO_3^- and MnO_4^- ($\tau_{зад}$ of less than 1 s) along with stable perchlorate ($\tau_{зад}$ of about 40 s).

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